REACTIVE ORGANOPOLYSILOXANE

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Equivalents:

Abstract

PURPOSE:To obtain a reactive organopolysiloxane having excellent weather resistance, thermal resistance and durability which is valuable as a modifier for inter-material adhesion by providing a structure comprising at least one specific organic reactive functional group, condensable silylalkyl group and polyoxyalkylene group in each molecule.

CONSTITUTION:The title compound has in its molecule a silicon atom and, directly bonded thereto, at least one organic reactive functional group (a) of formula I (wherein R<1> represents a direct bond or a 1-20C divalent hydrocarbon residue and X represents a functional group having an organic reactivity), at least one condensable silylalkyl group (b) of formula II (wherein R<2> represents a 2-5c alkylene group; each of R<3> and R<4> independently represents a hydrogen atom or a 1-5C alkyl group; and a is 2 or 3), and at least one polyoxyalkylene group (c) of formula III (wherein R<5> represents a hydrogen atom, an acyl group or a monovalent hydrocarbon residue; l or 0 or a positive integer; and each of m and n is 0 or a positive integer of 150 or less, provided that m+n in an integer of from 1 to 150).

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(54)【発明の名称】　反応性オルガノポリシロキサン

(57)【要約】

【構成】下式の反応性オルガノポリシロキサン〔Ｙ＝有機反応性官能基；Ｚ＝縮合性シリルアルキル基；Ｑ＝ポリオキシアルキレン基；Ｒ＝Ｈ，一価炭化水素基，ハロゲン化アルキル基；Ｍ＝Ｙ，Ｚ，Ｑ，Ｒ；ｏ＝０～５００；ｐ，ｑ，ｒ＝０～２００〕

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   R      R      R      R      R
   |      |      |      |      |
M-(SiO)o-(SiO)p-(SiO)q-(SiO)r-Si-M
   |      |      |      |      |
   R      Y      Z      Q      R
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【効果】親水性に優れ、２つの素材間（特に有機材と無機フィラー等の無機材間）の接着性改質剤、塗料改質剤、繊維の表面改質剤等として有用であり、優れた耐候性、耐熱性および耐久性を付与する。

【特許請求の範囲】

【請求項1】　1分子中に、ケイ素原子に直接結合した

a）次式：

$-R^1-X$

（式中、R^1 は直接結合または炭素原子数1ないし20の二価炭化水素基を表し、Xは有機反応性を有する官能基を表す）で表される有機反応性官能基と、

b）次式：

$$-R^2-\underset{\displaystyle (R^3)_{3-a}}{\underset{|}{Si}}-(OR^4)_a$$

（式中、R^2 は炭素原子数2ないし5のアルキレン基を表し、R^3 およびR^4 は互いに独立して水素原子または炭素原子数1ないし5のアルキル基を表し、aは2または3の整数である）で表される縮合性シリルアルキル基と、

c）次式：

$$-(CH_2)_l-O-(C_2H_4O)_m-(C_3H_6O)_n-R^5$$

（式中、R^5 は水素原子、アシル基または一価炭化水素基を表し、lは0または正の整数であり、mおよびnは0または150以下の正の整数であるが、ただしm＋nは1ないし150の整数である）で表されるポリオキシアルキレン基とをそれぞれ少なくとも1個有する反応性オルガノポリシロキサン。

【請求項2】　次式：

$$M-(\underset{R}{\overset{R}{SiO}})_o-(\underset{Y}{\overset{R}{SiO}})_p-(\underset{Z}{\overset{R}{SiO}})_q-(\underset{Q}{\overset{R}{SiO}})_r-\underset{R}{\overset{R}{Si}}-M$$

〔式中、Rは互いに独立して水素原子、一価炭化水素基またはハロゲン化アルキル基を表し、Yは次式：

$-R^1-X$

（式中、R^1 は直接結合または炭素原子数1ないし20の二価炭化水素基を表し、Xは有機反応性を有する官能基を表す）で表される有機反応性官能基を表し、Zは次式：

$$-R^2-\underset{\displaystyle (R^3)_{3-a}}{\underset{|}{Si}}-(OR^4)_a$$

（式中、R^2 は炭素原子数2ないし5のアルキレン基を表し、R^3 およびR^4 は互いに独立して水素原子または炭素原子数1ないし5のアルキル基を表し、aは2または3の整数である）で表される縮合性シリルアルキル基を表し、

Qは次式：

$$-(CH_2)_l-O-(C_2H_4O)_m-(C_3H_6O)_n-R^5$$

（式中、R^5 は水素原子、アシル基または一価炭化水素基を表し、lは0または正の整数であり、mおよびnは0または150以下の正の整数であるが、ただしm＋nは1ないし150の整数である）で表されるポリオキシアルキレン基を表し、Mは上記R、Y、ZおよびQから選択される基を表し、oは0ないし500の整数であり、pは0ないし200の整数であり、qは0ないし200の整数であり、rは0ないし200の整数であるが、ただしpが0の場合はMがYで、かつqおよびrはいずれも1以上の整数であり、qが0の場合はMがZで、かつpおよびrはいずれも1以上の整数であり、rが0の場合はMがQで、かつpおよびqはいずれも1以上の整数である〕で表される反応性オルガノポリシロキサン。

【請求項3】　Rが一価炭化水素基またはフロロアルキル基を表す請求項2記載の反応性オルガノポリシロキサン。

【請求項4】　素材間の接着性改質剤、塗料改質剤または繊維の表面改質剤として用いられる請求項1ないし3のいずれか1項に記載の反応性オルガノポリシロキサン。

【請求項5】　有機材と無機材との間の接着性改質剤として用いられる請求項4記載の反応性オルガノポリシロキサン。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は反応性オルガノポリシロキサンに関し、より詳しくは、素材間の接着性改質剤、塗料改質剤、繊維の表面改質剤等として有用であり、優れた耐候性、耐熱性および耐久性を示す新規な反応性オルガノポリシロキサンに関する。

【0002】

【従来の技術】1分子中にポリオキシアルキレン基と有機反応性官能基とを有するオルガノポリシロキサンは米国特許第4184004号に開示されている。また、1分子中にアルコキシシリル基と有機反応性官能基とを有するオルガノポリシロキサンは英国特許第1409741号に開示されている。しかしながら、これらのオルガノポリシロキサンを2つの素材間（特に有機材と無機フィラー等の無機材間）の接着性改質剤、塗料改質剤、繊維の表面改質剤等として使用する場合、前者では基材との反応性に劣り、後者では親水性のコントロールができ

ない等の欠点があった。

【0003】

【発明が解決しようとする課題】本発明は上記した欠点を解決するためになされたものであり、素材間（特に有機材と無機フィラー等の無機材間）の接着性改質剤、塗料改質剤、繊維の表面改質剤等として使用した場合に、優れた耐候性、耐熱性および耐久性を示す新規な反応性オルガノポリシロキサンを提供することを課題とする。

【0004】

【課題を解決するための手段】本発明者等は鋭意研究の結果、1分子中に、ケイ素原子に直接結合した、有機反応性官能基と縮合性シリルアルキル基とポリオキシアルキレン基をそれぞれ少なくとも1個有する反応性オルガノポリシロキサンにより上記課題が解決できることを見出し、本発明を完成させた。

【0005】すなわち、本発明は、1分子中に、ケイ素原子に直接結合した

a）次式：

$$-R^1-X$$

（式中、R^1 は直接結合または炭素原子数1ないし20の二価炭化水素基を表し、Xは有機反応性を有する官能基を表す）で表される有機反応性官能基（Y基）と、

b）次式：

$$-R^2-\underset{\displaystyle (R^3)_{3-a}}{\underset{|}{Si}}-(OR^4)_a$$

（式中、R^2 は炭素原子数2ないし5のアルキレン基を表し、R^3 およびR^4 は互いに独立して水素原子または炭素原子数1ないし5のアルキル基を表し、aは2または3の整数である）で表される縮合性シリルアルキル基（Z基）と、

c）次式：

$$-(CH_2)_l-O-(C_2H_4O)_m-(C_3H_6O)_n-R^5$$

（式中、R^5 は水素原子、アシル基または一価炭化水素基を表し、lは0または正の整数であり、mおよびnは0または150以下の正の整数であるが、ただしm＋nは1ないし150の整数である）で表されるポリオキシアルキレン基（Q基）とをそれぞれ少なくとも1個有する反応性オルガノポリシロキサンに関する。

【0006】本発明は特に次式：

$$M-(\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{Si}}O)_o-(\underset{\underset{\displaystyle Y}{|}}{\overset{\overset{\displaystyle R}{|}}{Si}}O)_p-(\underset{\underset{\displaystyle Z}{|}}{\overset{\overset{\displaystyle R}{|}}{Si}}O)_q-(\underset{\underset{\displaystyle Q}{|}}{\overset{\overset{\displaystyle R}{|}}{Si}}O)_r-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{Si}}-M$$

〔式中、Rは互いに独立して水素原子、一価炭化水素基またはハロゲン化アルキル基を表し、Yは次式：

$$-R^1-X$$

（式中、R^1 は直接結合または炭素原子数1ないし20の二価炭化水素基を表し、Xは有機反応性を有する官能基を表す）で表される有機反応性官能基を表し、Zは次式：

$$-R^2-\underset{\displaystyle (R^3)_{3-a}}{\underset{|}{Si}}-(OR^4)_a$$

（式中、R^2 は炭素原子数2ないし5のアルキレン基を表し、R^3 およびR^4 は互いに独立して水素原子または炭素原子数1ないし5のアルキル基を表し、aは2または3の整数である）で表される縮合性シリルアルキル基を表し、Qは次式：

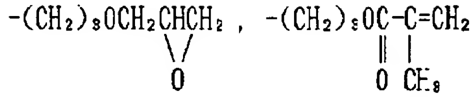
$$-(CH_2)_l-O-(C_2H_4O)_m-(C_3H_6O)_n-R^5$$

（式中、R^5 は水素原子、アシル基または一価炭化水素基を表し、lは0または正の整数であり、mおよびnは0または150以下の正の整数であるが、ただしm＋nは1ないし150の整数である）で表されるポリオキシアルキレン基を表し、Mは上記R、Y、ZおよびQから選択される基を表し、oは0ないし500の整数であり、pは0ないし200の整数であり、qは0ないし200の整数であり、rは0ないし200の整数であるが、ただしpが0の場合はMがYで、かつqおよびrはいずれも1以上の整数であり、qが0の場合はMがZで、かつpおよびrはいずれも1以上の整数であり、rが0の場合はMがQで、かつpおよびqはいずれも1以上の整数である〕で表される反応性オルガノポリシロキサンに関する。

【0007】上記式中、Rは互いに独立して水素原子、一価炭化水素基、例えばメチル基、エチル基、プロピル基、ブチル基、オクチル基、ドデシル基、フェニル基、フェネチル基等またはハロゲン化アルキル基、例えばトリフロロプロピル基、クロロプロピル基であるが、特に一価炭化水素基、とりわけメチル基、およびフロロアルキル基が好ましい。

【0008】上記Y基の中のR^1 は直接結合または炭素原子数1ないし20の二価炭化水素基、例えば$-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH(CH_3)CH_2-$, $-(CH_2)_4-$, $-(CH_2)_6-$, $-(CH_2)_8-$, $-CH_2CH_2C_6H_4-$, $-(CH_2)_{12}-$, $-(CH_2)_{16}-$であり、好ましくはプロピレン基である。また、Y基のXは有機反応性を有する官能基、例えばエポキシ基、アミノ基、水酸基、カルボキシル基、アシル基、メルカプト基、メタクリロ基、イソシアネート基、ウレイド基、ビニル基、アミド基、イミド基、イミノ基、アルデヒド基、ニトロ基、ニトリル基、オキシム基、アゾ基、ヒドラゾン基である。Y基の具体例としては、$-(CH_2)_3OH$, −

$(CH_2)_3SH$, $-(CH_2)_3NH_2$, $-(CH_2)_7COOH$,

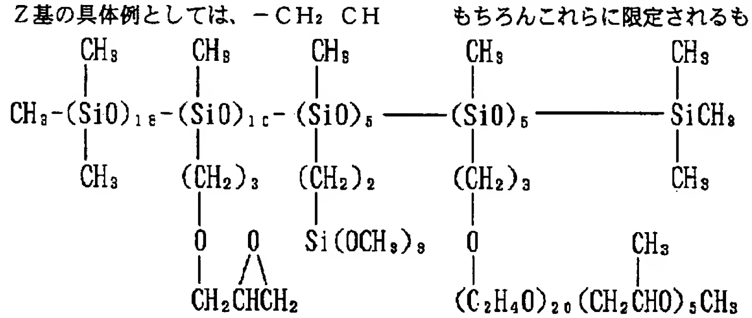


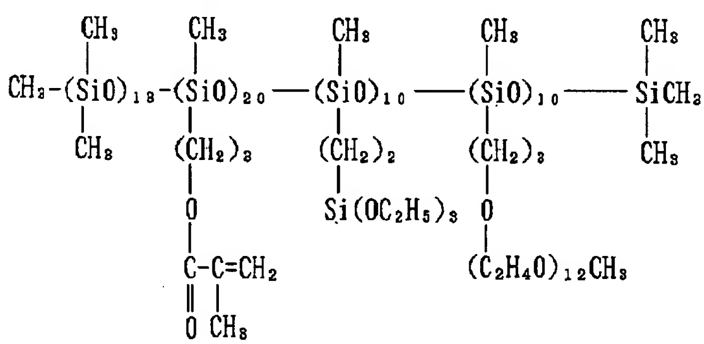
等を挙げることができるが、これらに限定されるものではない。

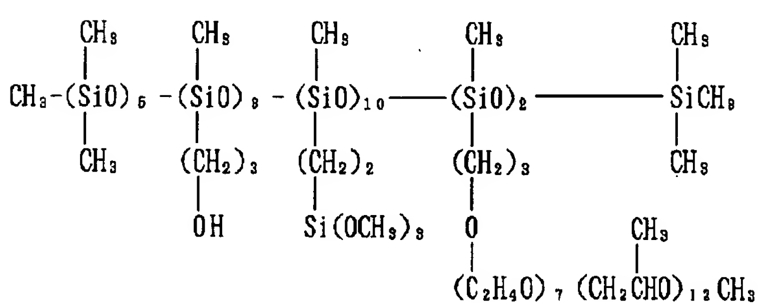
【0009】上記Z基の中のR[2] は炭素原子数2ないし5のアルキレン基、例えば$-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH(CH_3)CH_2-$, $-(CH_2)_4-$, $-(CH_2)_5-$等であり、好ましくはエチレン基である。R[3] およびR[4] は互いに独立して水素原子または炭素原子数1ないし5のアルキル基、例えばメチル基、エチル基、プロピル基、ブチル基であり、好ましくはR[3] はメチル基、R[4] はメチル基またはエチル基である。aは2または3の整数であるが、反応性の点から3が好ましい。Z基の具体例としては、$-CH_2CH_2Si(OCH_3)_3$, $-CH_2CH_2Si(OC_2H_5)_3$, $-CH_2CH_2Si(CH_3)(OCH_3)_2$, $-CH_2CH_2Si[OCH(CH_3)_2]_3$, $-(CH_2)_3Si(CH_3)(OC_2H_5)_2$, $-(CH_2)_5Si(C_2H_5)(OC_2H_5)_2$ 等を挙げることができるが、これらに限定されるものではない。

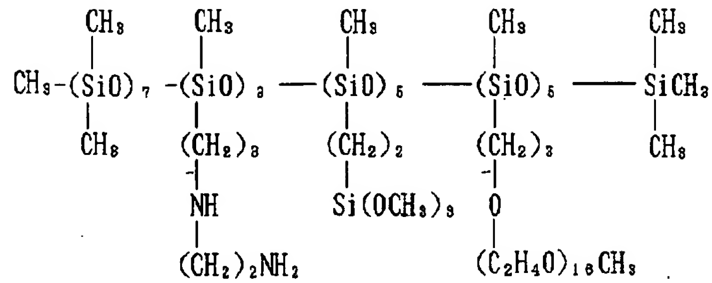
【0010】上記Q基の中のR[5] は水素原子、アシル基例えばアセチル基もしくはプロピオニル基、または一価炭化水素基例えばメチル基、エチル基、プロピル基、ブチル基、フェニル基もしくはビニル基であり、lは0または正の整数であり、mおよびnは0または150以下の正の整数であるが、ただしm+nは1ないし150の整数である。

【0011】本発明の反応性オルガノポリシロキサンの具体例としては、以下のものを挙げることができるが、もちろんこれらに限定されるものではない：


(1)


(2)


(3)



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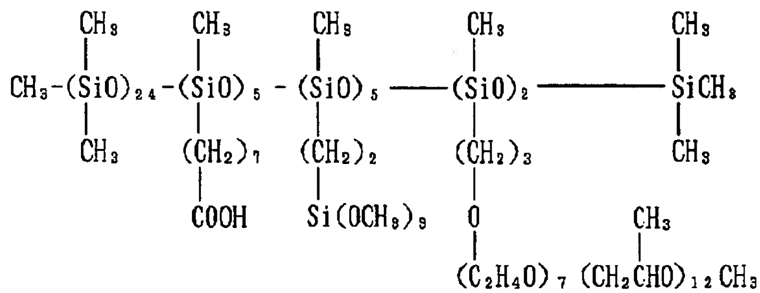

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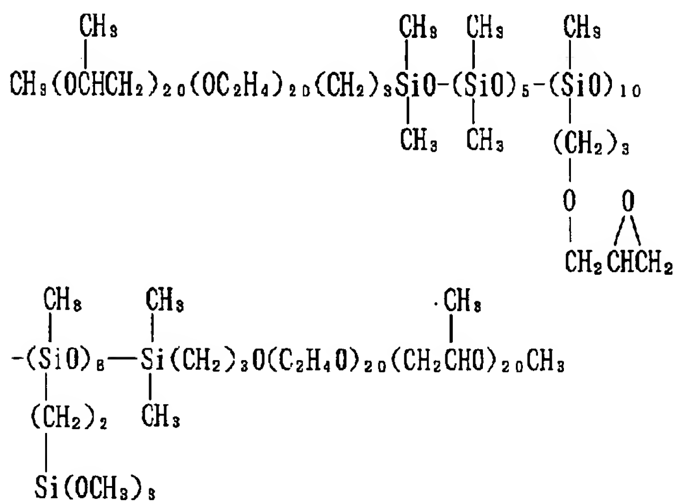
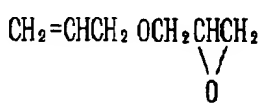
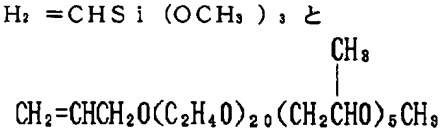


(6)

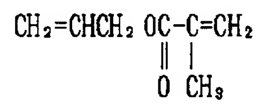
【0012】本発明の反応性オルガノポリシロキサンはそれ自体公知である従来の合成方法の組合せにより製造することができる。例えば、上記式（1）で表される化合物の場合、対応するメチルハイドロジェンポリシロキサンに



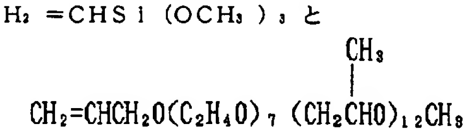
とCH₂ ＝CHSｉ（OCH₃）₃と



とを白金系触媒の存在下で付加反応させることによって得られる。同様に、上記式（2）で表される化合物の場合、対応するメチルハイドロジェンポリシロキサンに



とCH₂ ＝CHSｉ（OC₂ H₅ ）₃とCH₂ ＝CHCH₂ O（C₂ H₄ O）₁₂CH₃とを白金系触媒の存在下で付加反応させることによって得られる。さらに、上記式（3）で表される化合物の場合、対応するメチルハイドロジェンポリシロキサンにCH₂ ＝CHCH₂ OHとCH₂ ＝CHSｉ（OCH₃）₃と



とを白金系触媒の存在下で付加反応させることによって得られる。また、上記式（4）で表される化合物の場合、対応するメチルハイドロジェンポリシロキサンにCH₂ ＝CHCH₂ ＣｌとCH₂ ＝CHSｉ（OCH₃）

試験化合物		曲げ強度（ｐｓｉ）	
		硬化直後	７２時間煮沸後
ブランク		１５８００	９８００
本発明化合物	(A)	１８０００	１３２００
	(B)	１８６００	１５１００
	(C)	１６６００	１２５００
	(D)	１７７００	１３０００
対照化合物	(E)	１５３００	９２００
	(F)	１４９００	８８００

【００２２】

【発明の効果】本発明の反応性オルガノポリシロキサンは、そのケイ素原子に直接結合した、有機反応性官能基（Ｙ基）と縮合性シリルアルキル基（Ｚ基）とポリオキシアルキレン基（Ｑ基）をそれぞれ少なくとも１個有するものであり、十分な親水性を示す。従って、本発明の反応性オルガノポリシロキサンは水および水とアルコールの混合液に容易に溶解または分散するため、これが素材間（特に有機材と無機フィラー等の無機材間）の接着性の改質剤、塗料改質剤、繊維の表面改質剤等として使用された場合、確実にオルガノポリシロキサンは基材間に分散され、しかも優れた耐候性、耐熱性および耐久性を付与する。また、本発明の反応性オルガノポリシロキサンはその合成原料の多様性から、改質すべき各基材や各用途にあわせた多様な分子設計が可能で、設計どおりの特性を容易に付与できるものである。

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(54) [Title of the Invention] REACTIVE ORGANOPOLYSILOXANE

(57) [Abstract]

[Constitution] Reactive organopolysiloxane of the following formula (Y = organic reactive functional group; Z = condensing silyl alkyl group; Q = polyoxyalkylene group; R = H, monovalent hydrocarbon group, or halogenated alkyl group; M = Y, Z, Q, or R; o = 0 to 500; p, q, r = 0 to 200):

[see original for formula]

[Effects] Superior hydrophilic property; useful, for example, as an adhesive modifier between two materials (especially between an organic material and an inorganic material such as an inorganic filler), paint modifier, or fiber surface modifier; imparts superior weather resistance, heat resistance, and durability.

[Claims]

[Claim 1] Reactive organopolysiloxane that has at least one of each of the following bonded directly to silicon atoms within one molecule:

a) an organic reactive functional group represented by the following formula:

[see original for formula]

(where R^1 represents a direct bond or a bivalent hydrocarbon group with 1 to 20 carbon atoms, and X represents a functional group that has organic reactivity),

b) a condensing silyl alkyl group represented by the following formula:

[see original for formula]

(where R^2 represents an alkylene group that has 2 to 5 carbon atoms, R^3 and R^4 independently of each other represent a hydrogen atom or alkyl group with 1 to 5 carbon atoms, and a represents the integer 2 or 3), and

c) a polyoxyalkylene group represented by the following formula:

[see original for formula]

(where R^5 represents a hydrogen atom, acyl group, or monovalent hydrocarbon group, l represents 0 or a positive integer, and m and n represent 0 or a positive integer of 150 or less, but m + n equals an integer from 1 to 150).

[Claim 2] Reactive organopolysiloxane represented by the following formula:

[see original for formula]

(where R independently of each other represents a hydrogen atom, monovalent hydrocarbon group, or halogenated alkyl group, Y represents an organic reactive functional group represented by the following formula:

[see original for formula]

(where R^1 represents a direct bond or a bivalent hydrocarbon group with 1 to 20 carbon atoms, and X represents a functional group that has organic reactivity), Z represents a condensing silyl alkyl group represented by the following formula:

[see original for formula]

(where R^2 represents an alkylene group that has 2 to 5 carbon atoms, R^3 and R^4 independently of each other represent a hydrogen atom or alkyl group with 1 to 5 carbon atoms, and a represents the integer 2 or 3), Q represents a polyoxyalkylene group represented by the following formula:

[see original for formula]

(where R^5 represents a hydrogen atom, acyl group, or monovalent hydrocarbon group, l represents 0 or a positive integer, and m and n represent 0 or a positive integer of 150 or less, but m + n equals an integer from 1 to 150), M represents a group selected from the above-mentioned R, Y, Z, and Q, o is an integer from 0 to 500, p is an integer from 0 to 200, q is an integer from 0 to 200, and r is an integer from 0 to 200, but when p is 0, M is Y and both q and r are integers are integers of 1 or greater, when q is 0, M is Z and both p and r are integers of 1 or greater, and when r is 0, M is Q and both p and q are integers of 1 or greater).

[Claim 3] Reactive organopolysiloxane described in Claim 2 wherein R represents a monovalent hydrocarbon group or chloroalkyl group.

[Claim 4] Reactive organopolysiloxane described in any of Claims 1 through 3 used as an adhesive modifier between two materials, a paint modifier, or a fiber surface modifier.

[Claim 5] Reactive organopolysiloxane described in Claim 4 used as an adhesive modifier between an organic material and an inorganic material.

[Detailed Specifications]

[0001]

[Field of Industrial Use]

This invention pertains to a reactive organopolysiloxane. More particularly, this invention pertains to a novel reactive organopolysiloxane that is useful as an adhesive modifier between materials, a paint modifier, or a fiber surface modifier, and shows superior weather resistance, heat resistance, and durability.

[0002]

[Prior Art]

Organopolysiloxane that has a polyoxyalkylene group and an organic reactive functional group within one molecule is disclosed by United States Patent No. 4184004. In addition, organopolysiloxane that has an alkoxysilyl group and an organic reactive functional group within one molecule is disclosed by British Patent No. 1409741. However, when these organopolysiloxanes are used, for example, as adhesive modifiers between two materials (especially between an organic material and an inorganic material such as an inorganic filler), paint modifiers, or fiber surface modifiers, these have drawbacks such as poor reactivity with materials in the first case and inability to control hydrophilic property in the latter two cases.

[0003]

[Problems that the Invention is to Solve]

The problems addressed by this invention are to solve the drawbacks described above and offer a novel reactive organopolysiloxane that shows superior weather resistance, heat resistance, and durability when used, for example, as an adhesive modifier between materials (especially between an organic material and an inorganic material such as an inorganic filler), a paint modifier, or a fiber surface modifier.

[0004]

[Means of Solving the Problems]

As a result of extensive research, the present inventors discovered that the problems described above can be solved by a reactive organopolysiloxane that has at least one of each of an organic reactive functional group and a condensing silyl alkyl group bonded directly to silicon atoms within one molecule, and so achieved the present invention.

[0005]

That is, this invention pertains to reactive organopolysiloxane that has at least one of each of the following bonded directly to silicon atoms within one molecule:

a) an organic reactive functional group (group Y) represented by the following formula:

[see original for formula]

(where R^1 represents a direct bond or a bivalent hydrocarbon group with 1 to 20 carbon atoms, and X represents a functional group that has organic reactivity),

b) a condensing silyl alkyl group (group Z) represented by the following formula:

[see original for formula]

(where R^2 represents an alkylene group that has 2 to 5 carbon atoms, R^3 and R^4 independently of each other represent a hydrogen atom or alkyl group with 1 to 5 carbon atoms, and a represents the integer 2 or 3), and

c) a polyoxyalkylene group (group Q) represented by the following formula:

[see original for formula]

(where R^5 represents a hydrogen atom, acyl group, or monovalent hydrocarbon group, l represents 0 or a positive integer, and m and n represent 0 or a positive integer of 150 or less, but m + n equals an integer from 1 to 150).

[0006]

This invention especially pertains to reactive organopolysiloxane represented by the following formula:

[see original for formula]

(where R independently of each other represents a hydrogen atom, monovalent hydrocarbon group, or halogenated alkyl group, Y represents an organic reactive functional group represented by the following formula:

[see original for formula]

(where R^1 represents a direct bond or a bivalent hydrocarbon group with 1 to 20 carbon atoms, and X represents a functional group that has organic reactivity), Z represents a condensing silyl alkyl group represented by the following formula:

[see original for formula]

(where R^2 represents an alkylene group that has 2 to 5 carbon atoms, R^3 and R^4 independently of each other represent a hydrogen atom or alkyl group with 1 to 5 carbon atoms, and a represents the integer 2 or 3), Q represents a polyoxyalkylene group represented by the following formula:

[see original for formula]

(where R^5 represents a hydrogen atom, acyl group, or monovalent hydrocarbon group, l represents 0 or a positive integer, and m and n represent 0 or a positive integer of 150 or less, but m + n equals an integer from 1 to 150), M represents a group selected from the above-mentioned R, Y, Z, and Q, o is an integer from 0 to 500, p is an integer from 0 to 200, q is an integer from 0 to 200, and r is an integer from 0 to 200, but when p is 0, M is Y and both q and r are integers are integers of 1 or greater, when q is 0, M is Z and both p and r are integers of 1 or greater, and when r is 0, M is Q and both p and q are integers of 1 or greater).

[0007]

In the above-mentioned formulae, R independently of each other are a hydrogen atom, a monovalent hydrocarbon group such as methyl group, ethyl group, propyl group, butyl group, octyl group, dodecyl group, phenyl group, or phenetyl group, or a halogenated alkyl group such as trifluoropropyl group or chloropropyl group. However, monovalent hydrocarbon groups, particularly methyl group, and fluoroalkyl groups are especially preferred.

[0008]

R^1 in the above-mentioned group Y is a direct bond or a bivalent hydrocarbon group with 1 to 20 carbon atoms, such as $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH(CH_3)CH_2-$, $-(CH_2)_4-$, $-(CH_2)_6-$, $-(CH_2)_8-$, $-CH_2CH_2C_6H_4-$, $-(CH_2)_{12}-$, or $-(CH_2)_{16}-$, and preferably is a propylene group. X in group Y is a functional group that has organic reactivity, such as epoxy group, amino group, hydroxyl group, carboxyl group, acyl group, mercapto group, methacrylo group, isocyanate group, ureido group, vinyl group, amido group, imido group, imino group, aldehyde group, nitro group, nitryl group, oxime group, azo group, or hydrazine group. Concrete examples that can be cited of group Y include $-(CH_2)_3OH$, $-(CH_2)_3SH$, $-(CH_2)_3NH_2$, $-(CH_2)_7COOH$, $-(CH_2)_3OCH_2CHCH_2$, and $-(CH_2)_3OC-C=CH_2$, but are not limited to these.

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O　　　　　　　　O CH_3

[0009]

R^2 in the above-mentioned group Z is an alkylene group with 2 to 5 carbon atoms, such as $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH(CH_3)CH_2-$, $-(CH_2)_4-$, or $-(CH_2)_5-$, and preferably is an ethylene group. R^3 and R^4 independently of each other are a hydrogen atom or an alkyl group with 1 to 5 carbon atoms, such as methyl group, ethyl group, propyl group, or butyl group. Preferably, R^3 is a methyl group and R^4 is a methyl group or ethyl group. a is the integer 2 or 3, but in terms of reactivity, 3 is preferred. Concrete examples that can be cited of group Z include $-CH_2CH_2Si(OCH_3)_3$, $-CH_2CH_2Si(OC_2H_5)_3$, $-CH_2CH_2Si(CH_3)(OCH_3)_2$, $-CH_2CH_2Si[OCH(CH_3)_2]_3$, $-(CH_2)_3Si(C_2H_5)(OC_2H_5)_2$, but are not limited to these.

[0010]

R^5 in the above-mentioned group Q is a hydrogen atom, an acyl group such as acetyl group or propionyl group, or a monovalent hydrocarbon group such as methyl group, ethyl group, propyl group, butyl group, phenyl group, or vinyl group. l is 0 or a positive integer, and m and n are 0 or positive integers of 150 or less, but m + n equals an integer from 1 to 150.

[0011]

Concrete examples of reactive organopolysiloxanes of this invention that can be cited include the following, but are not limited to these:

[see original for formula] (1)

[see original for formula] (2)

[see original for formula] (3)

[see original for formula] (4)

[see original for formula] (5)

[see original for formula] (6)

[0012]

The reactive organopolysiloxane of this invention can be manufactured by synthesis methods by prior art that are themselves well known. For example, in the case of the compound represented by the above-mentioned Formula (1), this is obtained by addition-reacting

[see original for formula]

with the corresponding methylhydrogen polysiloxane in the presence of a platinum catalyst. Similarly, in the case of the compound represented by the above-mentioned Formula (2), this is obtained by addition-reacting $CH_2{=}CHCH_2OC{-}C{=}CH_2$, $CH_2{=}CHSI(OC_2H_5)_3$, and

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O CH_3

$CH_2{=}CHCH_2O(C_2H_4O)_{12}CH_3$ with the corresponding methylhydrogen polysiloxane in the presence of a platinum catalyst. Furthermore, in the case of the compound represented by the above-mentioned Formula (3), this is obtained by addition-reacting $CH_2{=}CHCH_2OH$,

CH_3

|

$CH_2{=}CHSI(OC_2H_3)_3$, and $CH_2{=}CHCH_2O(C_2H_4O)_7(CH_2CHO)_{12}CH_3$ with the corresponding methylhydrogen polysiloxane in the presence of a platinum catalyst. In addition, in the case of the compound represented by the above-mentioned Formula (4), this is obtained by addition-reacting $CH_2{=}CHCH_2Cl$, $CH_2{=}CHSi(OCH_3)_3$, $CH_2{=}CHCH_2O(C_2H_4O)_{16}CH_3$ with the corresponding methylhydrogen polysiloxane in the presence of a platinum catalyst, then reacting the product obtained with ethylenediamine.

[0013]

The reactive organopolysiloxane of this invention can be used, for example, as an adhesive modifier between two materials (especially between an organic material and an inorganic material such as an inorganic filler). This organopolysiloxane can be made the main

ingredient of an adhesive by using together with a natural rubber, a synthetic rubber such as styrene-butadiene copolymer rubber, butadiene rubber, isobutylene-isoprene copolymer rubber, chloroprene rubber, acrylonitrile-butadiene copolymer rubber, isoprene rubber, ethylene-propylene-diene copolymer rubber, or ethylene-propylene copolymer rubber, or a synthetic resin such as acrylonitrile-butadiene-styrene copolymer or polystyrene, or by blending with a rubber adhesive, urethane resin adhesive, or epoxy resin adhesive used when adhering these to other rubbers or resins. It also is effective as a surface adhesive between composites when blending rubbers and resins. Furthermore, the organopolysiloxane of this invention shows superior adhesive strength even when adhering organic materials such as the above-mentioned rubbers and resins to inorganic materials that include metals and inorganic fillers such as silica, quartz, talc, clay, zinc oxide, iron oxide, titanium oxide, aluminum oxide, calcium carbonate, aluminum hydroxide, mica, or carbon black, and obtains products such as reinforced plastics and high-strength elastomers that have high weather resistance and heat resistance. It also can be blended as a paint modifier with a paint resin comprised of a resin such as polyester resin or acrylic resin, and can obtain a coating that has superior weather resistance, durability, and heat resistance on surfaces such as metal, wood, or concrete. Furthermore, it may be applied as a fiber surface modifier to any type of fiber material, including natural fibers such as wool, silk, linen, cotton, or asbestos, regenerated fibers such as rayon, cupra, or acetate, organic synthetic fibers such as polyester, polyester ether, polyacrylonitrile, vinylon, polyvinylidene chloride, polyvinyl chloride, polyethylene, or polypropylene, and inorganic synthetic fibers such as fiberglass or carbon fiber. Moreover, fiber surfaces can be treated in any form, such as weaves, knits, non-woven cloth, or resin-worked fiber, with the result that properties such as weather resistance and durability are imparted to said fiber. Therefore, this invention pertains to use of the above-mentioned reactive organopolysiloxane of this invention as an adhesive modifier between materials, a paint modifier, and a fiber surface modifier. Of these, ideally, the organopolysiloxane of this invention is used as an adhesive modifier between organic materials and inorganic materials.

[0014]

[Working Examples]

Next, this invention is explained in greater detail based on working examples, but this invention is not limited to these.

[0015]

Working Example 1

80 g methylhydrogen polysiloxane represented by the following formula:

[see original for formula]

200 g toluene, and 10% ethanol solution of chloroplatinic acid such that platinum content was 20 ppm were placed in a 1000 ml three-neck flask fitted with a mechanical agitator, condenser, thermometer, and nitrogen inlet. 22.8 g vinyl trimethoxysilane and 35.1 g γ-glycidoxy-1-propene were added gradually to this mixture at high speed so as to maintain the temperature at 80 to 100°C. Agitation was continued for 2 hours while maintaining this temperature, and the system was reacted. Furthermore, 230 g of allyl polyether represented by the following formula:

[see original for formula]

were added gradually to this reaction mixture at high speed so as to maintain the temperature at 80 to 100°C. Completion of this reaction was evaluated by whether the test of $AgNO_3$ to SiH was negative. Next, the reaction mixture was neutralized with $NaHCO_3$, then filtered. When solvent was removed by a rotary evaporator at 50°C and 1 mm Hg, 312 g organopolysiloxane represented by the following formula were obtained:

[see original for formula] (A)

[0016]

Working Example 2

When the same operations as in Working Example 1 were performed using 300 g methylhydrogen polysiloxane represented by the following formula:

[see original for formula]

200 g toluene, 11.6 g vinyl trimethoxysilane, 3.6 g γ-glycidoxy-1-propene, 14.3 g allyl polyether represented by the following formula: $CH_2=CHCH_2O(C_2H_4O)_7CH_3$, and 10% ethanol solution of chloroplatinic acid such that platinum content was 20 ppm, 309 g organopolysiloxane represented by the following formula were obtained:

[see original for formula] (B)

[0017]

Working Example 3

When the same operations as in Working Example 1 were performed using 200 g methylhydrogen polysiloxane represented by the following formula:

[see original for formula]

200 g toluene, 100 g vinyl trimethoxysilane, 12 g allyl alcohol represented by the following formula: $CH_2=CHCH_2OH$, 175 g allyl polyether represented by the following formula: :

[see original for formula]

and 10% ethanol solution of chloroplatinic acid such that platinum content was 20 ppm, 330 g organopolysiloxane represented by the following formula were obtained:

[see original for formula] (C)

[0018]

Working Example 4

When the same operations as in Working Example 1 were performed using 100 g methylhydrogen polysiloxane represented by the following formula:

[see original for formula]

200 g toluene, 55 g vinyl trimethoxysilane, 73 g allyl methacrylate, 209 g allyl polyether represented by the following formula: $CH_2=CHCH_2O(C_2H_4O)_{12}CH_3$, and 10% ethanol solution of chloroplatinic acid such that platinum content was 20 ppm, 362 g organopolysiloxane represented by the following formula were obtained:

[see original for formula] (D)

[0019]

The following tests were conducted using the organopolysiloxanes of this invention represented by Formulae (A) to (D) synthesized in Working Examples 1 to 4 and organosiloxanes represented by the following Formulae (E) and (F) as controls for comparison:

[see original for formula] (E)

[see original for formula] (F)

[0020]

Test 1

10 g of any of the test compounds of Formulae (A) to (F) were added to 100 g isopropyl alcohol aqueous solution (water/isopropyl alcohol = 1/9) and blended until completed dispersed. 1.0 kg quartz powder was placed in a Henschel mixer, the test compound solution described above was added at a speed of 25 to 30 mL/min over several minutes while agitating evenly, and agitation and blending were continued for 30 minutes after addition was completed. After blending, the moistened quartz powder was removed, moved to a drying tray made of aluminum (40 cm x 40 cm x 5 cm), spread evenly to a thickness of 2 to 3 cm, and dried in a forced circulation dryer at 105°C for 1 hour. 1.0 kg Bakelite polyethylene DYNH, 1.0 kg quartz powder treated as described above, and 30 g Dicup (manufactured by Hercules) were blended at 121°C. Next, this was compression-molded at 177°C for 20 minutes, and the tensile strength of the molded product was measured. Results are shown below, but molded products that used organopolysiloxanes of this invention showed extremely high tensile strength compared to the blank and the controls.

Test Compound		Tensile Strength (psi)
blank		1700
Invention Compound	(A)	2500
	(B)	2300
	(C)	2100
	(D)	2100
Control Compound	(E)	1300
	(F)	1500

[0021]

Test 2

500 g Bakelite epoxy resin ERL-2774, 400 g methyl nadic [as transliterated] anhydride (curing agent), 2.5 g benzyldimethylamine (catalyst), 10 g test compound, and 500 g wollastonite (calcium silicate) were blended. Next, this was cured at room temperature for 16 hours, then cured at 177°C for 2 hours. Flexural strength was found immediately after curing and after boiling 72 hours. Results are shown below, but products according to this invention showed

extremely high flexural strength compared to the blank and the controls both immediately after curing and after boiling 72 hours, and in particular, showed a low rate of reduction in flexural strength after boiling 72 hours.

Test Compound		Flexural Strength (psi) immediately after curing	Flexural Strength (psi) after boiling 72 hours
Blank		15800	9800
Invention Compound	(A)	18000	13200
	(B)	18600	15100
	(C)	16600	12500
	(D)	17700	13000
Control Compound	(E)	15300	9200
	(F)	14900	8800

[0022]

[Effects of the Invention]

The reactive organopolysiloxane of this invention has at least one of each of an organic reaction functional group (group Y), a condensing silyl alkyl group (group Z), and a polyoxyalkylene group (group Q), and shows adequate hydrophilic property. Therefore, because the reactive organopolysiloxane of this invention dissolves or disperses easily in water or water and alcohol mixtures, when this is used as an adhesive modifier between materials (especially between an organic material and an inorganic material such as an inorganic filler), a paint modifier, or a fiber surface modifier, the organopolysiloxane disperses securely between the materials and imparts superior weather resistance, heat resistance, and durability. In addition, because of its varied synthesis ingredients, the reactive organopolysiloxane of this invention can take on various molecular designs to fit different base materials to be modified or different applications, and can easily impart characteristics according to the design.